

Combined Upgrading of Coal and Petroleum Residua

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This investigation examines the feasibility of using heavy petroleum crudes and residua as solvents in coal liquefaction. The concept being explored is to determine if coal and heavy petroleum crudes and residua can be simultaneously processed with mutual upgrading of both materials. Previous work by Moschopedis and coworkers¹⁻⁴ has examined the liquefaction of coal using Athabasca oil sands bitumen, Lloydminster heavy oil, Coker gas oil and Cold Lake bitumen. The effectiveness of these materials as hydrogen donor solvents and their thermal stability under liquefaction conditions was also examined. The effects of process parameters on the production of reaction products was also investigated. Other investigations have been performed by Mochida and coworkers⁵ in which several coals were liquefied in the presence of a Khafji vacuum residue. Other studies by Mochida^{6,7} have included the liquefaction of an Australian brown coal in a prehydrogenated petroleum pitch and the liquefaction of subbituminous coals using pyrene and various Ashland pitches.

This study examines the conversion of a bituminous coal to soluble products through coprocessing with six heavy petroleum crudes and residua. These reactions were performed thermally, in an inert and in a hydrogen atmosphere, and catalytically in a hydrogen atmosphere. The petroleum materials used range from a whole crude to a variety of residua. Chemical and physical characterizations have been performed to determine what factors are most influential in producing the end product. To determine the sensitivity of coprocessing to reaction conditions and to determine the most optimal parameters, an evaluation of key reaction parameters has been performed.

Experimental

Feedstock. Six petroleum crudes and residua, supplied by Cities Service Research and Development Company, have been examined for potential use as solvents for coal liquefaction processing. Analysis of the petroleum feedstocks are given in Table 1. The coals used in this study are a high volatile bituminous Illinois #6 coal, a Blacksville mine coal and a subbituminous coal, Clovis Point from Wyoming.

Screening Experiment. Screening experiments were performed at 400°C using a nitrogen atmosphere and a hydrogen atmosphere. Catalytic screening experiments with a hydrogen atmosphere were performed at 400° and 425°C. The equipment and reaction conditions used in these experiments were: a 50 cc stainless steel tubing bomb reactor, reaction time of 30 minutes, agitation at 860 cpm, and a solvent to coal ratio of 2:1. The reaction products were analyzed by a solvent separation scheme in which the product is successively extracted by pentane, benzene and methylene chloride/methanol. The liquid fractions obtained are oil (pentane solubles), asphaltenes (benzene soluble, pentane insolubles), and preasphaltenes (benzene insoluble, methylene chloride/methanol solubles), and insoluble organic matter. The weight of gases produced was also determined.

Parametric Evaluation. The reaction parameters evaluated as to their effect on coal conversion and product distributions from combined processing were reaction temperature, initial hydrogen reaction pressure, reaction time and diffusional pathlength of the catalyst. The reaction conditions for these evaluations are summarized below:

Reaction ConditionsParameter

	<u>Temperature</u>	<u>Pressure</u>	<u>Time</u>
Time	30 minutes	30 minutes	---
Temperature	----	425°C	425°C
Pressure	1250 psig H ₂	----	1250 psig
Agitation Speed	860 cpm	860 cpm	860 cpm
Coal	3 g, Illinois #6 or 3 g, Blacksville	3 g, Illinois #6	3 g, Illinois #6
Solvent	6 g, Maya Crude	6 g, Maya Crude	6 g, Maya Crude
Catalyst	None	1 g, Presulfided Shell 324 NiMo/Al ₂ O ₃ powdered (from 1/32" extrudates)	3 conditions were used: a. None Presulfided b. Shell 324 NiMo/Al ₂ O ₃ 1/16" extrudates c. Presulfided Shell 324 NiMo/Al ₂ O ₃ (from 1/16" extrudates)

The effect of thermal and catalytic combined processing on the reaction products from Clovis Point coal was also evaluated.

Characterization of the Petroleum Crudes and Residua. The petroleum crudes and residua were characterized by elemental analysis, molecular weight by vapor phase osmometry in pyridine, viscosity, Conradson Carbon, proton distribution, and specific gravity. Table 1 presents a composite of the physical and chemical characteristics of the petroleum crudes and residua.

Results and Discussion

Six heavy petroleum crudes and residua have been used as solvents in a series of coal liquefaction experiments to determine their ability to liquefy coal. The experiments were performed at 400° and 425°C using Illinois #6 coal and in three different environments: (1) a N₂ atmosphere, (2) a H₂ atmosphere and (3) and H₂ atmosphere using a pelletized presulfided NiMo/Al₂O₃ catalyst.

Analyses of the solvents using a solubility extraction procedure developed for coal materials showed that the petroleum crudes were between ~80% to 90% soluble in pentane and the pentane insoluble materials were mostly benzene solubles, asphaltenes. The coal derived solvent CPDU-200A was ~85% pentane soluble with the remainder being asphaltenes. The petroleum solvents have hydrogen to carbon ratios of ~1.45 to 1.65 and sulfur contents between 2.8% and 4.6%.

Liquefaction in a Nitrogen Atmosphere. Liquefaction experiments were performed in a hydrogen deficient, nitrogen atmosphere to determine how readily the hydrogen-rich petroleum solvents could transfer hydrogen directly to coal, thereby converting coal to a soluble product. The ability of tetralin and coal-derived CPDU-200A to convert coal was also determined.

Coal conversion obtained using tetralin was 57.5%, by CPDU-200A was 51.5%, and the most converted by a petroleum crude was 36.0%. At 400°C, the coal conversion in the petroleum materials range from 28% to 36%. These data indicate and the proton distribution as determined proton nuclear magnetic resonance (¹HNMR) substantiate that the petroleum crudes and residua do not contain hydrogen which can be easily

donated to coal. In fact, the majority of the protons in the petroleum materials lie in the alkyl β and γ regions. In these experiments, tetralin, a known hydrogen donor, was the only solvent that produced an increase in oils above that present in the original 2:1 solvent/coal mixture. In the hydrogen deficient atmosphere, donor hydrogen as present in hydroaromatic compounds, appears to be necessary for both coal conversion and the production and maintenance of the oil fraction. Similar results using model hydroaromatic and aliphatic solvents are present in the literature.⁸⁻⁹

Compared to the original product distribution, the reaction products from the combined processing lost pentane solubles. A general increase in the asphaltene content of the product liquids was observed as compared with the original charge. In the hydrogen deficient environment, both the coal and the heavy petroleum materials may undergo polymerization forming coke-like material which appears as IOM. In addition, the reacting coal may incorporate a significant portion of the petroleum soluble material into the coal matrix.

Noncatalytic Experiments with a Hydrogen Atmosphere. To eliminate some of the possible retrogressive reactions of the petroleum materials and the coal associated with the inert atmosphere, a hydrogen atmosphere was used. As with the nitrogen atmosphere, tetralin converted the most coal, yielding 71.2%, while the coal-derived material CPDU-200A converted 56.8%. Compared to the nitrogen atmosphere, substantially more coal was converted in the hydrogen atmosphere with the petroleum solvents. The coal conversion ranged from ~43% to 54% depending upon the petroleum material used. The hydrogen atmosphere also either maintained or increased the oil yield as compared to the original charge. Three of the less viscous lighter petroleum materials, Maya Crude, West Texas TLR and Mayan TLR showed a positive increase in oil; whereas, in nitrogen, each of these crudes showed a reduction in oil content when compared to the original solvent. Kuwait resid, West Texas vacuum short and West Texas TLR showed the greatest oil production improvement (> 7%) when a hydrogen rather than a nitrogen atmosphere was used.

Catalytic Liquefaction Using a Hydrogen Atmosphere. The effect of adding a presulfided $\text{NiMo}/\text{Al}_2\text{O}_3$ extrudate catalyst on the conversion of coal and on reaction products has also been investigated. The reactions were performed at 400°C and 425°C. For all the solvents used, the addition of presulfided $\text{NiMo}/\text{Al}_2\text{O}_3$ increased both oil production and coal conversion. In the compilation of data presented in Table 2, it is apparent that at 400°C and 425°C the presence of the $\text{NiMo}/\text{Al}_2\text{O}_3$ hydrogenation catalyst caused a significant improvement in the oil yield. The same improvement is observed in coal conversion. In those cases where the catalytic reactions were performed at both 400°C and 425°C, the twenty-five (25) degree rise in temperature seemed to be a secondary effect on both coal conversion and oil yield with the possible exception of the West Texas vacuum short resid. For West Texas vacuum short resid, coal conversion seemed to be affected by temperature both in catalytic and noncatalytic reactions with hydrogen atmospheres. The addition of a hydrogenation catalyst can significantly improve the oil production and coal conversion in combined processing.

Chemical and Physical Properties of the Petroleum Crudes and Residua. Among the six petroleum materials individual differences are apparent in their ability to convert coal and produce pentane soluble materials. A number of chemical and physical properties of the petroleum materials have been evaluated and are given in Table 1. A typical coal liquid, CPDU-200A, is also shown in Table 1 and has been used as a point of comparison between the coal-derived and petroleum solvents.

From these analyses, general comments can be made concerning the properties of the petroleum solvents. Each petroleum crude and residuum contains large asphaltenic compounds as evidenced by a lack of solubility of ~6 to ~20% of the petroleum material in pentane and that much solubility in benzene. All of the petroleum solvents are hydrogen-rich and high in sulfur as compared to coal-derived liquids.

The typical hydrogen to carbon ratio for coal-derived liquids is 1.0 or less; all of the petroleum crudes and residua used in this study have H/C ratios in the range of 1.45 to 1.65. The ash levels in the petroleum crudes range from 0.012 wt % for West Texas vacuum short resid to 0.082 wt% for Mayan topper long resid. This low ash content is insignificant in this work in terms of the product distribution obtained after coprocessing with coal. All of the petroleum solvents are highly aliphatic, having f_a values between 0.32 and 0.37. Proton distributions of the petroleum solvents show the protons to be primarily alkyl β and γ protons. Few hydroaromatic protons are present. CPDU-200A, by contrast, is quite aromatic, having a f_a value of 0.71. A higher percentage of cyclic alpha protons are present in the CPDU-200A than in any of the petroleum materials. The aromatic nature and the presence of some hydroaromatics may account for the CPDU-200A's ability to convert more coal than do the petroleum solvents.

Coal conversion in the petroleum solvents using a hydrogen atmosphere at 400°C can be correlated with the viscosity of the petroleum material and with the Conradson Carbon number. The highly viscous solvents, Kuwait resid and West Texas vacuum short resid, give less coal conversion than do the less viscous petroleum solvents. The petroleum solvents with lower Conradson Carbon numbers promote higher coal conversion. A similar trend is observed with molecular weight. The petroleum solvents with lower molecular weights, Lloydminster reduced crude, West Texas TLR, Maya Crude and Mayan TLR, correlate with increased coal conversion. West Texas TLR which has the lowest Conradson Carbon and the second lowest molecular weight and viscosity gives the highest coal conversion of any of the petroleum solvents during coprocessing. The addition of a catalyst changes the order of the coal conversion among the six petroleum solvents and apparently the relative importance of the solvent's properties. No obvious correlations exist between the abovementioned solvent properties and coal conversion when a catalyst is used.

Parametric Evaluation. The effect of reaction conditions on combined coal and heavy residua processing has been evaluated using the parameters of reaction temperature, initial hydrogen pressure, reaction time and diffusional pathlength of the catalyst. For these studies, Maya Crude was used as the solvent. Three coals were used, Illinois #6, Blacksville, and Clovis Point, with Illinois #6 coal being used for the majority of the experiments. Solvent extraction of Illinois #6 at room temperature showed the coal to be ~90% insoluble at room temperature. When reacted at 425°C in hydrogen in the absence of a solvent, ~35% of Illinois #6 coal was converted, primarily to preasphaltenes. Under the same conditions, ~46% of the Clovis Point was converted with all solubility fractions being present. The upgradability of the Maya Crude was also examined to determine if the asphaltenes present could be upgraded to oil. After thermal reaction the Maya Crude did not change substantively although 2.7% of the product was gas. A 4% increase in oil was observed on catalytic hydrogenation with a further increase in gas production.

Effect of Temperature on the Product Distribution from Illinois #6 and Blacksville Coals. To determine the effect of reaction temperature on the product distributions from coprocessing, the reactions were performed at 375°, 400°, 425°, 450° and 475°C. With increasing temperatures, oil production and higher coal conversion were observed for both coals up to a temperature of 425°C where a maximum in oil yield and a minimum of IOM occurred. For both coals, the greatest coal conversion was observed at 425°C. At higher temperatures, 450° - 475°C, higher gas yields and IOM yields (lower coal conversion) are observed for both coals. Based on these data, a temperature of 425°C was selected for combined processing.

Effect of Initial Hydrogen Pressure on Coprocessing. To determine the sensitivity of combined processing to initial hydrogen pressure, the initial hydrogen pressure was increased from 0 psig to 1500 psig. A powdered Shell 324 NiMo/Al₂O₃ was added to the reaction mixture. The products distributions shown in Figure 1 demonstrate the need for a hydrogen environment to convert coal and simultaneously to upgrade the petroleum crudes. When no hydrogen is present, only 8.6% coal conversion is

observed. Comparing this conversion to that of thermally reacted coal with no solvent in a hydrogen atmosphere, the hydrogen atmosphere increases coal conversion by more than 20%. In a hydrogen deficient atmosphere, the petroleum solvent may also be undergoing retrogressive reactions forming coke-like materials adding to the IOM. At an initial hydrogen pressure of 250 psig, the pentane solubles produced were higher than that in the original mixture; coal conversion was 52.5%, suggesting that even low levels of hydrogen can be effective in reducing the number of retrogressive reactions when solvent and catalyst are present to aid in the transfer of hydrogen to coal. At 500 psig, the coal conversion again increased significantly to 78.7% while the pentane soluble yields increased to 70.4%. As the hydrogen pressure was increased even further, coal conversion continued to climb yielding 86.9% at 1500 psig. The oil produced also increased at 1500 psig to 78.5%. Above 500 psig, the rate of increase for both coal conversion and pentane soluble yields was lower than between 0 and 500 psig.

Effect of Time and Catalyst Diffusion Pathlength on Product Distributions from the Liquefaction of Illinois #6 Coal. To determine the effect of time on combined processing, three sets of experiments were performed: (1) thermal reaction with no catalyst present, (2) NiMo/Al₂O₃ pelletized catalysts, and (3) NiMo/Al₂O₃ powdered catalysts.

A comparison of the ability of Maya Crude to convert coal under these three conditions is given in Figure 2. For all three cases, long reaction time, 90 minutes, increased coal conversion when compared to the shorter time experiments. The use of powdered catalyst increased the amount of coal conversion substantially compared to the thermal and catalyst pellet experiments. This increase occurred for all reaction times. The coal conversion in the thermal and extrudate experiments are very similar and are about 20% less than the powdered catalyst.

From these experiments, it is apparent that the longer residence time the coal has in a hydrogen atmosphere the more coal will be converted. The use of a catalyst increases the availability of the hydrogen to the coal and increases the rate of coal dissolution. The use of a powdered catalyst makes hydrogen more available to the coal by providing contact between the catalyst particles and the dissolving coal matrix. This increased availability is caused by decreasing the diffusional pathlength required for the coal to traverse before coming into contact with an active hydrogenation site.

Hydrogen consumption in the thermal and in both catalytic experiments increased with increasing time. The coprocessing experiments using the powdered catalyst consumed more hydrogen than did either the experiments using pellets or no catalyst. The hydrogen consumption data correlate with the yields of pentane solubles produced under the three conditions. More pentane solubles were produced in the powdered catalyst experiments than in the extrudate experiments which was more than the thermal. The data is presented in Figure 3 which shows the oil production from the three cases as a percentage of the upgradable material present in the reaction, the upgradable material being defined as the maf coal and petroleum asphaltenes present at the beginning of the reaction. The catalyst obviously aids in oil production, with the powdered form yielding significantly greater oil production than the extrudate pellets. These data are a clear indication of the influence of pore diffusional restrictions in limiting the oil yield with extrudate pellets.

Illinois #6 coal was also liquefied in tetralin with a powdered catalyst for 30 minutes. The coal conversion obtained was 92.4% and the oil production was 86.7%. Both the coal conversion and oil production are higher in tetralin than in Maya Crude under equivalent reaction conditions. The values obtained from the combined processing are 81.6% and 76.7%, respectively. Longer reaction times of 90 minutes with Maya Crude produce higher yields of coal conversion and oil, 83.4% and 82.7%, respectively.

The effect of thermal and catalytic combined processing from Clovis Point coal was also evaluated. The product distributions obtained from 30 minutes of reaction are given in Table 4. The product distributions from Clovis Point coal from the three reaction conditions show similar trends to those obtained from Illinois #6 coal. Oil production and coal conversion increased with catalytic treatment, the highest yields being produced from the powdered catalyst. For comparable reaction times, coal conversion from Clovis Point was slightly higher than Illinois #6 for the thermal and pelletized catalyst case. Oil production from Clovis Point coal was consistently 5 to 6% higher than Illinois #6 coal.

Summary and Conclusions

Petroleum crudes and residua and coal have been coprocessed at typical liquefaction conditions in atmospheres of nitrogen and hydrogen and in the presence of hydrogen and a catalyst. At 400°C coal conversion in a nitrogen atmosphere was low and at the same level as the thermal coal reaction with no solvent, indicating that no transfer of hydrogen from the petroleum solvents to the coal occurred. Coal conversion increased in the presence of hydrogen; further increases in coal conversion were observed in the presence of catalyst at 400°C and 425°C. The dominant factor of the increased conversion in the majority of the heavy petroleum materials was the presence of the catalyst with the 25° temperature rise being a secondary effect. Oil production from combined processing showed negative or level yields in the N₂ atmosphere, level or slightly positive yields in the H₂ atmosphere and for most petroleum solvents significant increases when a catalyst and hydrogen were both present. As in the case of coal conversion, the catalyst appears to be the dominant factor in the increase with temperature having a secondary effect.

Individual differences among the petroleum solvents are observed in the product distributions obtained from combined processing. Coal conversion in the H₂ atmosphere appears to be correlated with viscosity, molecular weight and Conradson Carbon number of the petroleum crude. These particular solvent characteristics do not seem as important in coal conversion when a catalyst is present.

The parametric evaluation has shown that optimal conditions for combined processing are:

- Reaction Temperature: 425°C
- Hydrogen Pressure: above 500 psig initial hydrogen pressure
- Time: 90 minutes
- Catalyst: powdered hydrogenation catalyst

Coal conversion and oil production from combined catalytic (powdered) processing compare favorably with that from tetralin with a powdered catalyst. Comparison of the final oil yields to the initial charge shows that combined processing yields a net oil increase of 23.3% for 90 minute reaction while tetralin provides a net oil increase of 17.7% for 30 minutes of reaction.

Table 1. Analysis of Liquefaction Solvents

Solvents	Product Distribution (wt%)				Ash, wt%	Elemental Analysis				
	Oil	Asphaltenes	Preasphaltenes	10M		C	H	N	S	H/C
Maya Crude	84.4	15.6			0.058	84.6	11.5	1.21	3.09	1.63
West Texas TLR	93.6	6.4			0.033	86.4	11.0	0.34	2.80	1.51
Mayan TLR	79.5	20.5			0.082	85.3	10.8	0.51	4.19	1.51
Lloydminster Reduced Crude	84.0	16.0			0.039	85.0	10.7	0.34	4.35	1.49
Kuwait Resid	88.96	10.99	0.05		0.031	79.5	10.3	0.19	4.63	1.55
West Texas Vacuum Short Resid	88.7	11.3			0.012	86.1	10.4	0.44	3.33	1.47
CPDU-200A	85.48	12.47	1.16	0.89		89.3	7.3	1.20	0.56	0.97
Solvents	Molecular Weight	f_a	η_D	Viscosity (poise)	Specific Gravity	%API		Conradson Carbon		
Maya Crude	577	0.32	1.52		0.920	22.3		10.41		
West Texas TLR	545	0.35	1.55	28.2	0.979	13.0		10.34		
Mayan TLR	668	0.37	1.56	317	1.000	10.0		15.87		
Lloydminster Reduced Crude	481	0.36	1.57	389	1.004	9.44		14.23		
Kuwait Resid	961	0.34	1.58	3470	1.014	8.05		17.00		
West Texas Vacuum Short Resid	922	0.35	1.58	7075	1.014	8.05		17.33		
CPDU-200A		0.71								

Table 2. Effect of Atmosphere and Catalyst on Oil Production and Coal Conversion

Oil, Wt %	Tetralin	Maya Crude	West Texas		Mayan TLR	Lloydminster Reduced Crude	Kuwait Resid	West Texas		CPDU 200A
								Vacuum	Short	
Original	67.5	56.9	63.2	53.7	56.7	60.0	59.8	57.7		
N ₂ , 400°C	70.6	58.7	60.4	53.2	55.7	56.0	54.0	53.4		
H ₂ , 400°C	71.2	59.9	65.8	56.4	58.8	60.4	58.4	56.3		
H ₂ + cat, 400°C		69.2			68.1		64.0			
N ₂ , 425°C		58.2			51.5					
H ₂ , 425°C		62.0	65.1		62.2		58.1			
H ₂ + cat, 425°C	83.1	72.3	73.7	66.3	71.5	68.2	66.9	73.8		
Average Conversion, %										
N ₂ , 400°C	57.2	28.4	30.2	34.9	28.4	30.2	26.7	50.3		
H ₂ , 400°C	70.6	49.8	53.5	49.3	48.9	45.2	44.5	56.6		
H ₂ + cat, 400°C		67.3			72.1		52.9			
N ₂ , 425°C		28.9			13.2					
H ₂ , 425°C		62.5			64.7		58.5			
H ₂ + cat, 425°C	81.0	66.2	68.9	62.3	75.2	69.2	65.4	81.6		

Table 3. Hydrogen Distributions in Petroleum and Coal-Derived Solvents

Solvents	% Condensed Aromatics	% Uncondensed		% Cyclic α	% Alkyl α	% Cyclic β	% Alkyl β	% γ
		Aromatics	Plus Hydroxyl					
Maya Crude	1.7		2.2	7.2	5.5	16	44	23
West Texas	3.1		1.2	6.1	4.9	17	46	21
Mayan TLR	3.6		3.0	7.1	5.9	15	43	22
Lloydminster								
Reduced Crude	5.9		2.6	8.5	6.5	18	38	20
Kuwait	4.6		2.0	7.3	6.6	17	45	18
West Texas								
Vacuum Short	7.0		0.0	14	7.0	29	33	9.9
CPDU-200A	35		13	17	12	8.8	9.7	5.3

Table 4. Product Distribution of Clovis Point Coal Reacted in Maya Crude Under Thermal and Catalytic Conditions

Product Distribution, wt%	Thermal	Catalyst	
		Pellets	Powder
Gas	5.7	5.7	4.9
Oil	68.4	75.0	81.1
Asphaltenes	9.0	5.5	5.1
Preasphaltenes	5.2	4.9	2.9
IOM	11.7	8.9	6.0
% Coal Conversion	62.3	71.6	80.8

Reaction Conditions: 30 minutes, 1250 psig initial H₂ pressure, agitation 860 cpm, 425°C.

References

1. Moschopedis, S. E., Fuel, 590, 1980, 67.
2. Moschopedis, S. E., Hawkins, R. W., Fryer, J. F. and Speight, J. G., Fuel, 59, 1980, 647.
3. Moschopedis, S. E., Hawkins, R. W. and Speight, J. G., ACS Fuel Preprints, 26, (3), 1981, 131.
4. Moschopedis, S. E., Hawkins, R. W. and Speight, J. G., Fuel Processing Technology, Vol. 5, 1982, 213.
5. Mochida, I., Takanabe, A. and Takeshita, K., Fuel, 58, 1979, 17.
6. Mochida, I., Moriguchi, Y., Korai, Y., Fujitsu, H., and Takeshita, K., Fuel, 60, 1981, 746.
7. Mochida, I., Iwamoto, K., Tahara, T., Korai, Y., Fujitsu, A. and Takeshita, K., Fuel, 61, 1982, 603.
8. Neavel, R., Fuel, 1976, 55, 237.
9. Curtis, C. W., Guin, J. A., and Kwon, K. C., AIChE National Meeting, paper 62b, November, 1982.

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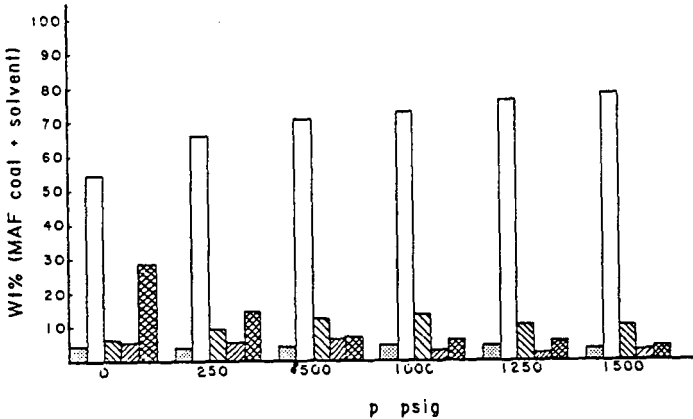


Figure 1. Effect of Initial Hydrogen Pressure on Product Distributions from Combined Processing of Illinois #6 and Maya Crude.

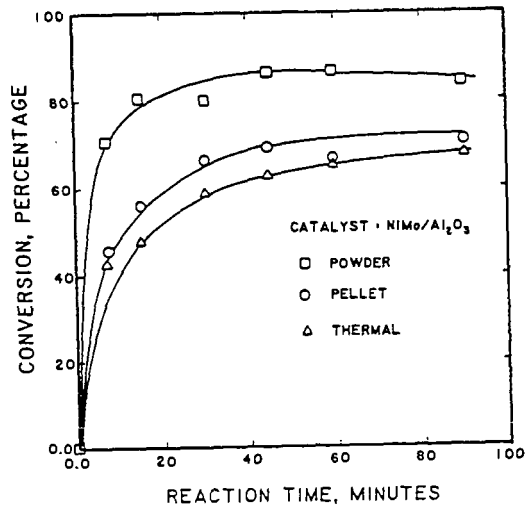


Figure 2. Effect of Time and Catalyst on Coal Conversion from Combined Processing of Illinois #6 Coal and Maya Crude.

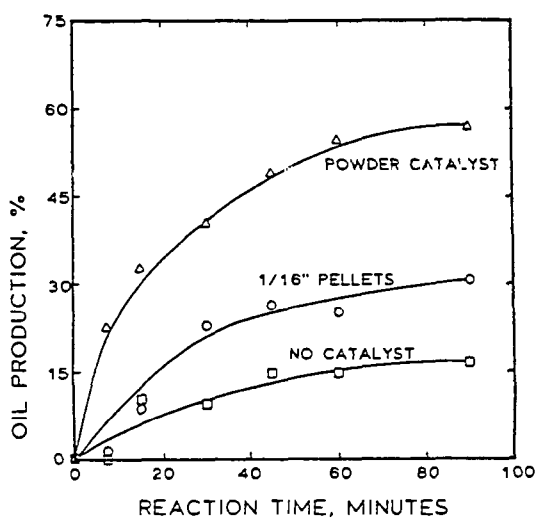


Figure 3. Effect of Time and Catalyst on Oil Production from Combined Processing of Illinois #6 Coal and Maya Crude.